Comment

Comments on "Controlling reaction selectivity in the oxidation of methanol at Cu(110) surfaces"

[by P.R. Davies and G.G. Mariotti]

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In the previous paper Davies and Mariotti [1] report the production of formate from co-dosing methanol and oxygen on Cu(110). The point of this letter is to confirm and expand on their report using the technique of scanning tunnelling microscopy (STM) and to make some comments on aspects of their paper.

In earlier papers we contended that little or no formate is produced on Cu(110) by sequential dosing of oxygen and then methanol [2,3] the major reaction pathway being methanol conversion to methoxy which decomposes above $\sim$ 340 K to formaldehyde. Definite evidence for this comes from our own work using temperature-programmed desorption (TPD) [4] in which the CO_2 desorption peak intensity (arising from formate decomposition) at 480 K following methanol dosing onto oxygen precovered Cu(110) was compared with that produced by formic acid dosing which generates a known formate coverage; this indicated conversion of $\sim$ 2% of methoxy to formate. This compares favourably with the small ratio of desorption peaks from formate versus methoxy decomposition in the work of, for instance, Russell et al. on Cu(111) [5] and Fu and Somorjai [6] on Cu(110). In addition, spectroscopic interrogation of sequentially dosed (oxygen then methanol) single-crystal Cu surfaces indicates that methoxy is the only reaction product at 300 K [7,8], however if left "overnight" in UHV some formate may be produced on Cu(110) [8]. There is no doubt, however, that the exact details of dosing temperature, pressure and time of exposure will affect the amount of formate produced, since, at the simplest level, formate production is competitive with formaldehyde desorption, assuming (as Davis and Mariotti do) that formate derives from formaldehyde oxidation in the following scheme:

$$2CH_3OH + O_{(a)} \rightarrow 2CH_3O_{(a)} + H_2O_{(g)} \quad (1)$$

$$CH_3O_{(a)} \rightarrow H_2CO_{(a)} \quad (2)$$

$$H_2CO_{(a)} \rightarrow H_2CO_{(g)} \quad (3)$$

$$H_2CO_{(a)} + O_{(a)} \rightarrow H_2COO_{(a)} \quad (4)$$

$$H_2COO_{(a)} \rightarrow HCOO_{(a)} + H_{(a)} \quad (5)$$

Indeed the previous paper of Davis and Mariotti and other recent publications from that group report varying yields of formate under different sequentially dosed conditions and propose different mechanisms in each case [8,9]; formaldehyde oxidation and methane elimination from two methoxy molecules. Furthermore, the statement of Davies and Mariotti, "The accepted mechanism for methanol oxidation at copper surfaces ... has only recently been updated to include oxidation to formate" (steps 4 and 5 above, their step 5) is quite incorrect, having been proposed originally by Wachs and Madix [10] and more recently by Bowker et al. [11–13] for various copper surfaces, including catalysts. The fundamental studies which directly describe formaldehyde oxidation as a facile reaction on Cu(110) were reported 15 years ago [14].

We have recently published several papers relating to the sequential dosing experiment, using molecular beam studies and STM, describing the reaction steps involved and showing minimal formate production [3,15]. In the last year at Reading we have extended this work using an Oxford Instruments high-temperature STM and have employed it to carry out co-dosing experiments which have been reported recently at conferences [16,17].

In our STM co-dosing experiments we exposed a clean Cu(110) surface at 300 K to gas phase mixtures of methanol and oxygen of differing composition at approximately the same pressure, 10^{-7} to 10^{-8} mbar. The reaction was followed in real time by imaging the surface during exposure. The evolution of the reaction differed for significantly different gas phase compositions in general agreement with the work of Davies et al.

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For oxygen-rich mixtures ($O_2 : CH_3OH > 1.4 : 1$) the (2×1) reconstruction characteristic of oxygen on Cu(110) was seen to grow preferentially while methanol attacked terminal oxygen atoms to produce adsorbed methoxy with a (5×2) structure (eq. (1)) in small, long (in the $\langle 001 \rangle$ direction) islands. We did not observe any adsorbed formate which would be identified by appearance of one of a number of structures including c(2×2) which formate is known to produce from previous experiments involving formic acid adsorption on Cu(110) [18]. We would therefore agree with Davies' remark "In an oxygen-rich mixture, chemisorbed oxygen island growth is favoured and formate formation inhibited". For methanol-rich mixtures ($O_2 : CH_3OH < 1 : 5$) a complete methoxy (5×2) layer slowly forms from methanol reaction with adsorbed oxygen, eq. (1), the clean surface having a negligible sticking coefficient for methanol. The slow buildup of methoxy was determined by the low rate of oxygen adsorption on the surface. Continued exposure transformed areas of the overlayer to the c(2×2) structure characteristic of formate, as shown in fig. 1. In fact, great care has to be taken to remove all traces of oxygen contaminants from the methanol in order to avoid significant formate production. Such contamination is often difficult to measure due to the methanol mass 32 amu cracking fraction, which is common to the major oxygen fragment. Fig. 2 shows small patches of (2×1) oxygen and c(2×2) formate in an island of methoxy, after prolonged exposure to a 3 : 1 mixture of $CH_3OH : O_2$. Before observation of the oxygen and formate structures the surface again consisted entirely of methoxy, while longer exposures resulted in conversion of methoxy to long chains of alternating oxygen (2×1) and formate c(2×2) islands directed along the $\langle 001 \rangle$ azimuth. Thus, a scheme of methanol oxidation is as shown in fig. 3 similar to those reported previously [11–13]. Methanol can be oxidised through to CO_2 and H_2/H_2O (the latter depending on the oxidation

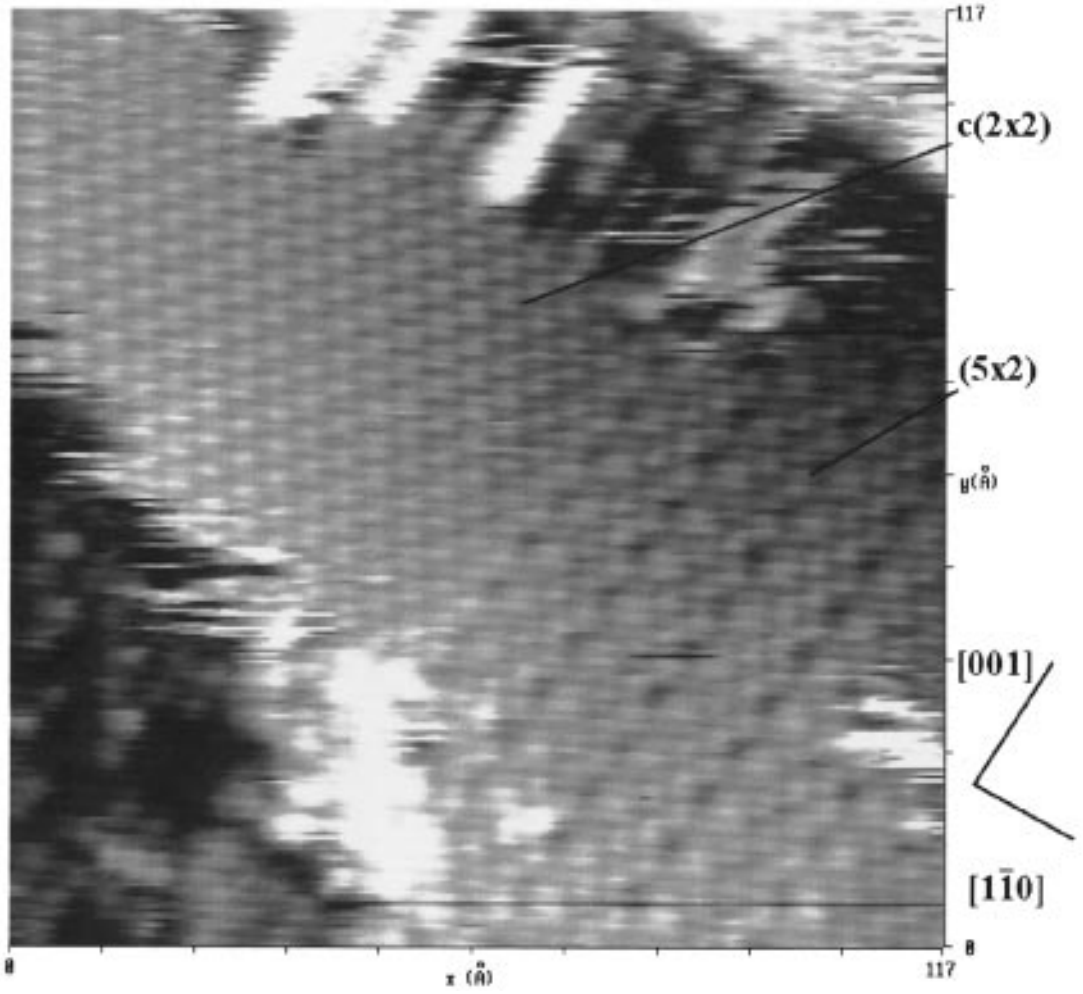

Fig. 1. Formate c(2×2) grown alongside the methoxy (5×2) structure as a result of co-dosing a methanol-rich mixture of methanol and oxygen ($CH_3OH : O_2 \approx 5 : 1$). Imaged at 1 nA with -2 V sample bias across a 117 Å square area.

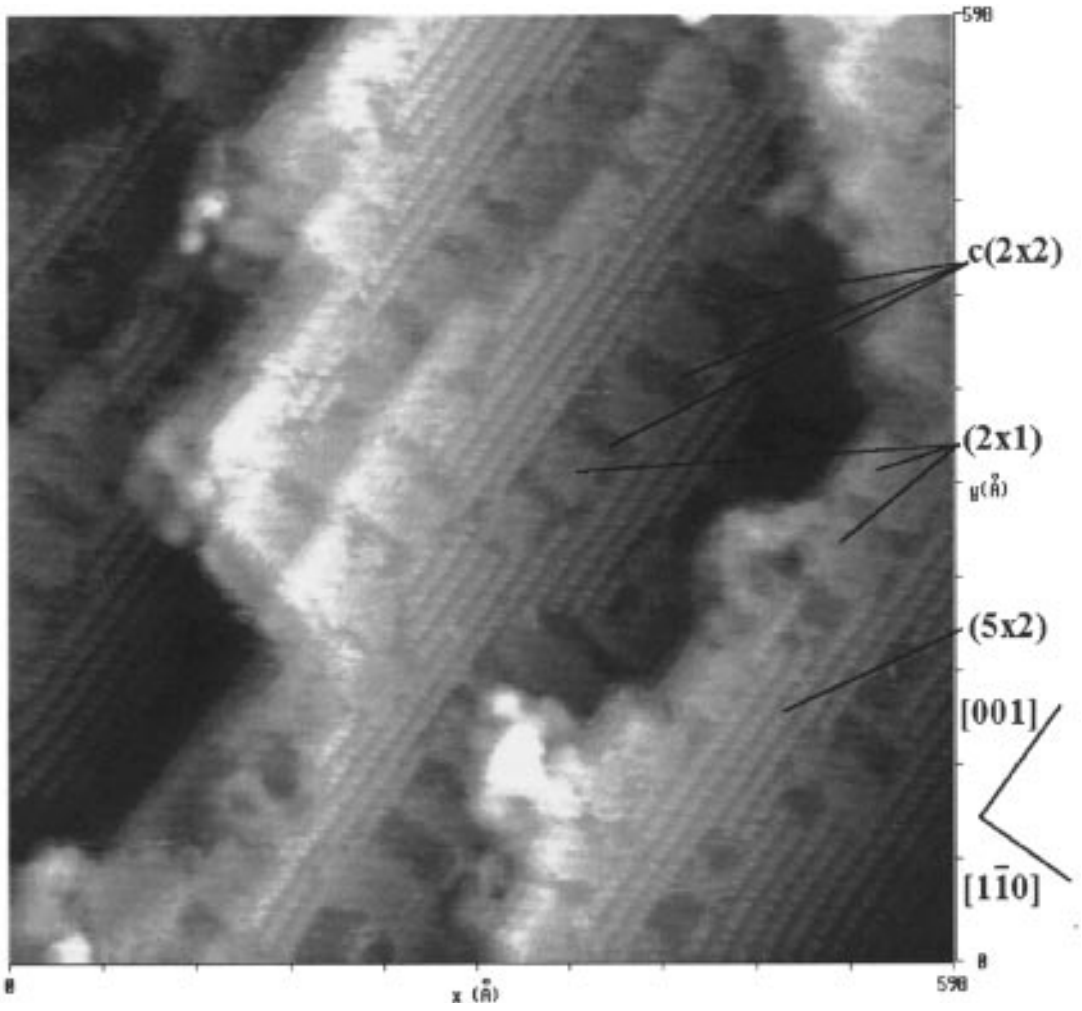

Fig. 2. Segregated alternating islands of oxygen (2 × 1) and formate c(2 × 2) within the methoxy (5 × 2) overlayer as a result of co-dosing a mixture of $CH_3OH : O_2 \approx 3 : 1$. A complete methoxy (5 × 2) layer forms initially and continued dosing converts small areas of the surface into the formate oxygen island structure. Further dosing extends the alternating formate oxygen islands across the surface in the ⟨001⟩ direction. Imaged at −500 mV and 1 nA across a 598 Å square area.

state of the surface), essentially the reverse of the methanol synthesis scheme.

From our STM data it is important to note the strong dependence of the surface composition with time for a given $CH_3OH : O_2$ ratio. In their paper Davies and Mariotti report the relative selectivity of the reaction toward formaldehyde or formate production as a function of the $CH_3OH : O_2$ ratio for a fixed exposure. As our results show, this would produce a somewhat arbitrary selectivity depending upon which point the reaction had reached at the given exposure. This is also apparent in their TPD data as the *total* desorption yield (methoxy + formate decomposition peaks) varies strongly with gas composition. A further point raised in the paper of Davies and Mariotti is that "TPD cannot distinguish easily between a pure formate adlayer and a mixed chemisorbed oxygen and methoxy adlayer that converts to formate during the TPD ramp". This point is particularly important as one of the authors also claims in a previous publication [9] that significant formate production occurs from a sequential dosing experiment at 300 K thus bringing into question the difference between the sequential and co-dosing experiments proposed by Davies and co-workers. Fortunately, our STM data *do* demonstrate that formate production occurs at 300 K. Significantly for intermediate mixture compositions ($MeOH : O_2$ of 3 : 1) formate is accompanied by the growth of small segregated oxygen (2 × 1) islands, as can be seen in fig. 2, which could lead to increased formate production during a TPD temperature ramp as Davies and co-workers suggest [9]. Despite these reservations there is considerable agreement between the conclusions drawn from the TPD work of Davies and Mariotti and our STM data. Clearly formate production is enhanced during co-dosing relative to sequential dosing and is particularly sensitive to gas phase composition and we agree

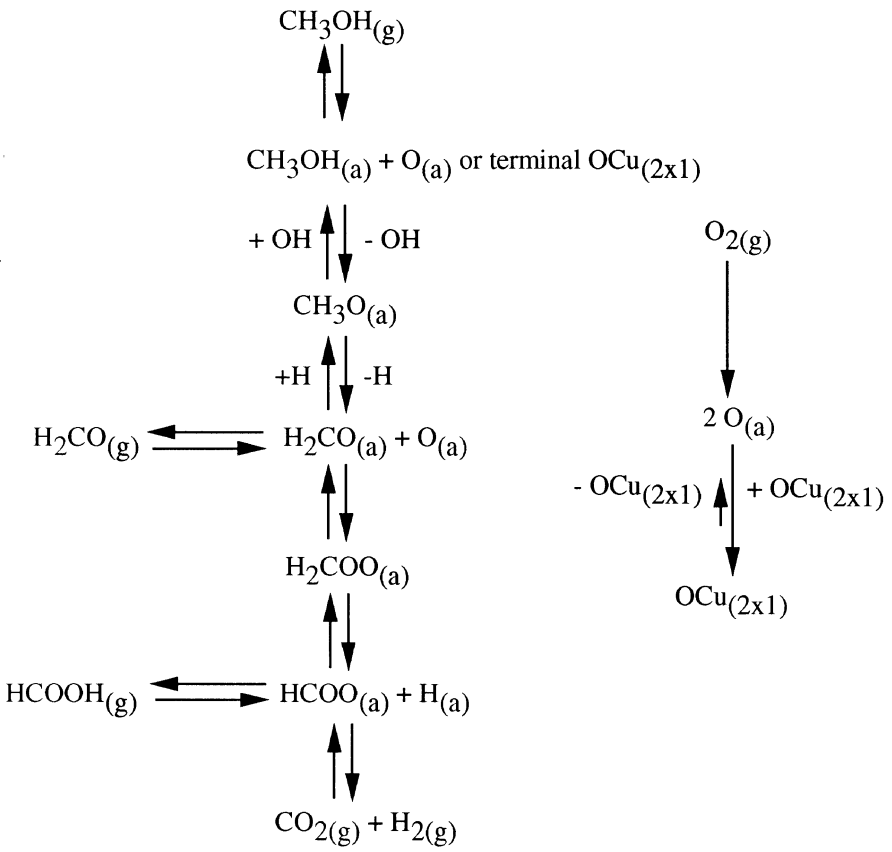

Fig. 3. A schematic reaction network for methanol oxidation on the Cu surface showing the variety of intermediates involved. By co-dosing, the surface density of $O_{(a)}$ (isolated adsorbed O atoms) remains high due to the continued dissociation of oxygen gas on the clean surface. Thus the reaction may proceed from formaldehyde through the di-oxymethylene intermediate to formate. In contrast, a sequentially dosed surface initially contains little $O_{(a)}$ but a high coverage of the oxygen (2×1) reconstruction, $OCu_{(2\times1)}$, allowing methoxy formation only at the terminal sites of the O–Cu rows which constitute this structure. During a TPD temperature ramp of such a surface $O_{(a)}$ may be formed by thermal evaporation from the $OCu_{(2\times1)}$ and some formate produced. This would also be increased by employing deuterated methoxy due its higher decomposition temperature.

that the co-dosing methodology allows for differing selectivity as a result of more reactive oxygen species playing a role in the overall reaction. An interesting point of commonality is that the reaction is poisoned by growth of oxygen (2×1) islands which capture the reactive oxygen adatoms. The reconstructed oxygen islands, which may be considered a surface oxide, are extremely unreactive toward formate synthesis. It must be noted, however, that the reaction of methanol through to formate has been reported on copper oxide surfaces [11,12,19]. Under these circumstances the dominant surface species are ionic copper and oxygen, though no doubt defects in the adlayer play a very important role in the reaction.

To conclude, it must be said that methanol oxidation on copper is an extremely complex reaction involving several organic intermediates, several configurations of adsorbed oxygen and considerable surface reconstruction including large-scale transport of Cu atoms/ions across the surface [20]. The relative importance of each of these factors will be strongly temperature and pressure dependent, as is the case for most catalytic reactions. Nevertheless, this system represents a fascinating model for surface reaction studies, and will hopefully continue to present a rich medium for debate and controversy.

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